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DETECTION OF TRITIUM IN STORAGE VAULTS CONTAINING RH TRU WASTE AT THE IDAHO NATIONAL ENGINEERING AND ENVIRONMENTAL LABORATORY

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ABSTRACT

Waste drums containing remote-handled (RH) transuranic (TRU) waste from the Argonne National Laboratory-East (ANL-E) are stored in sealed, underground vaults at the Radioactive Waste Management Complex (RWMC) at the Idaho National Engineering and Environmental Laboratory (INEEL). The waste consists of laboratory debris from the destructive examination of fuel elements irradiated mostly in the Experimental Breeder Reactor II (EBR-II). In 2004, air samples were obtained from some of these vaults and analyzed for radioactivity. Some of the samples show that the vaults contained several DAC's (derived air concentrations) of tritium, which are considered as non-negligible by Environmental Protection Agency (EPA) regulations.

Based on Acceptable Knowledge (AK) records of the waste stored in the vaults, ORIGEN2 calculations were performed to estimate the isotopic contents in the waste drums stored in the vaults. The calculations are based on the irradiation of fuel elements that produced the waste. The absolute amounts of isotopic contents in the waste drums are normalized to Cs-137 contents derived from measured surface dose rates, mostly from the Cs-137 radiation, as documented in AK records. The amounts of tritium thus calculated (assuming no loss from those produced during fission except for decay) are compared to the measured values in the air samples from the vaults. The ratio of measured tritium in the form of tritiated water vapor to un-reduced tritium from fission is found to be from below detection levels to approximately 0.2%, but mostly in the range around 1×10^{-4} to 1×10^{-3}. It appears that even the debris from cutting and grinding the fuel elements contained substantial amounts of tritium, which were subsequently released from the fuel particles during years of storage in the vaults.

INTRODUCTION

The Intermediate Level Transuranic Storage Facility (ILTSF) at the Radioactive Waste Management Complex (RWMC) at the Idaho National Engineering and Environmental Laboratory (INEEL) has in its storage approximately 600 30-gal waste drums from the Argonne National Laboratory-East (ANL-E). The waste is composed of debris from the destructive examination of fuel elements (cutting, grinding, and polishing the fuel samples) irradiated mostly in the Experimental Breeder Reactor-II (EBR-II) at the Argonne National Laboratory-West (ANL-W) from the 1970's to the mid-1990's. The storage facility consists of sealed underground vaults. As plans for disposing of the waste drums in the Waste Isolation Pilot Plant (WIPP) get underway, the vaults will be opened and the drums retrieved and put in aboveground storage before their shipment to WIPP.

Among the safety concerns in opening the vaults are the presence of volatile organic compounds, gaseous hydrogen from radiolysis of organic material, and gaseous radionuclides in the enclosed atmosphere of the vaults. This paper addresses the measurements of tritium in the atmospheres of the vaults and the origin of the tritium as a fission product in the waste contaminated with irradiated fuel particles.

In the following sections, brief descriptions of the vaults are provided, followed by descriptions of the measurement method and results. The measurement results are then compared to the calculated amounts of tritium in the waste assuming that all the tritium generated from fission stayed with the fuel particles present in the waste (total tritium). The ratio between the measured tritium and total tritium would indicate the fraction of tritium in the fuel particles that was released to and retained in the vault atmosphere.

ILTSF VAULT DESCRIPTION

At the beginning of year 2004, there were approximately 140 underground vaults at the ILTSF that stored waste containers containing remote-handled (RH) transuranic (TRU) waste. The waste containers consist of 30- and 55-gal drums, and also some slender canisters (1 ft by 6 ft). The waste came from a variety of sources, including ANL-E, ANL-W, the Naval Reactor Facility (NRF), and the Test Reactor Area (TRA) at the INEEL. A common characteristic of the waste is that it all contains debris contaminated with irradiated fuel particles. Among the waste containers, there were approximately 600 30-gal drums containing waste from the Alpha-Gamma Hot Cell Facility (AGHCF) at ANL-E containing debris from destructive fuel examination. For these drums, good Acceptable Knowledge (AK) information is available, particularly relating to their surface dose rates, which were measured and recorded when the drums were packaged. For the other drums (ANL-W, NRF, and TRA), acceptable knowledge information has mostly not been gathered and they will be omitted in the paper.

The ANL-E waste drums are approximately 20 in. in diameter and 30 in. high. They were all stored in 24-in. diameter vaults, which have depths ranging from 10.5 ft to 27.5 ft in the drum storage space, have a concrete plug above the storage space for shielding, and have a bolted closure plate above the concrete plug. Because of the closure plate, the vaults are essentially air-tight. The number of drums in each vault ranges from two to eleven, but is mostly five.

ANL-E Waste Drum Storage Information

The storage vaults are labeled by column and row, such as A-56, meaning vault in column A and row 56. Air samples from thirty one (31) vaults that contained only ANL-E waste drums were obtained in 2004 and measured for tritium concentrations. Based on AK information [1], the maximum contact dose rates for the drums in these vaults, measured at the time of packing, were used to estimate the Cs-137 contents in these drums, which will be used later in this paper to estimate the tritium co-produced with the Cs-137 when the fuel elements were irradiated. For the ANL-E 30-gal drums, based on MicroShield [2] calculations, 1 Ci of Cs-137 (which accounts for more than 95% of the radiation dose) gives a contact dose rate of approximately 4 R/hr. The 4 R/hr per Ci of

Cs-137 conversion factor for each drum is used to estimate the Cs-137 contents of the vaults. Table I shows the data for these vaults.

Table I. Storage vault content information.

Vault ID	Number of drums	Vault depth (ft)	Drum package date	Sum of dose rates of drums on package date (R/hr)	Estimated Cs-137 content in vault on pack date (Ci)
E-6	4	10.5	10/19/95	15.2	3.8
E-7	4	10.5	10/13/95	31.7	7.9
E-8	4	10.5	10/23/95	14.1	3.5
C-9	5	13	09/13/78	33.0	8.3
C-11	5	13	08/21/78	13.9	3.5
C-15	10	27.5	11/20/81	132.5	33.1
C-16	11	27.5	02/16/81	74.0	18.5
B-17	11	27.5	12/18/80	52.2	13.0
C-17	11	27.5	08/29/80	65.3	16.3
C-18	11	27.5	09/21/80	120.6	30.1
C-21	4	10.5	08/04/81	33.7	8.4
F-26	5	13	09/19/83	17.5	4.4
C-51	5	13	06/25/88	71.0	17.8
A-52	5	13	09/28/90	25.8	6.5
B-52	5	13	09/24/90	73.1	18.3
C-52	5	13	09/25/90	10.5	2.6
A-53	5	13	09/27/90	25.5	6.4
B-53	5	13	10/04/90	18.1	4.5
C-53	5	13	10/03/90	49.1	12.3
A-54	5	13	10/09/90	45.8	11.5
B-54	5	13	10/11/90	10.5	2.6
C-54	5	13	09/03/80	19.8	5.0
A-55	5	13	05/21/92	27.9	7.0
B-55	5	13	05/23/92	43.8	10.9
C-55	2	13	09/06/80	4.8	1.2
A-56	5	13	05/08/93	28.8	7.2
B-56	3	13	04/25/93	61.0	15.3
C-56	2	13	05/01/93	38.0	9.5
A-57	5	13	05/06/93	49.7	12.4
C-57	5	13	05/14/93	25.8	6.4
C-58	5	13	05/20/93	29.3	7.3

AIR SAMPLING AND TRITIUM MEASUREMENT

During 2004, air samples were obtained from the ILTSF storage vaults by removing the threaded cap on the sample port (located on the vault lid) and inserting a tygon tube from the sampling device into the vault headspace. This allowed access into the inner volume of the vault without removing the vault lid. The following assumptions were made relevant to the sampling approach:

- Tritium within the vault is in the form of tritiated water vapor. Tritium is found in two phases, molecular T_2 and tritiated water vapor (HTO).

- Tritium concentration in the headspace is the same as that in the rest of the vault. Engineering drawings of the vaults show that the vault headspace is not physically isolated from the rest of the vault.

Tritium in the form of tritiated water vapor was sampled using a bubbler. A tritium bubbler consists of two fritted samplers, a pump, and tygon tubing for connections. A picture of the samplers and the pump is shown in Figure 1. A cap containing a long and a short stainless tube was inserted into each sampler. Vacuum from the pump was applied (using tygon tubing) to the short tube of the first sampler. The long tube of the first sampler was connected to the short tube of the next sampler. A section of tygon tubing was attached to the long tube of the second sampler and served as the sample input line. The first sampler served as a water trap to help prevent water from entering the pump. A known volume of water (typically 100 to 150 ml) was put into the second sampler. The pump was calibrated to an air flow rate of 1 liter per minute (lpm). The timer on the pump was set to 5 minutes for a total volume of 5 liters. This was more than an adequate volume to detect tritium concentrations less than the radiologically significant 0.3 DAC. One DAC (derived air concentration) is defined as 20 pCi/cm^3, so 0.3 DAC equates to 6 pCi/cm^3.

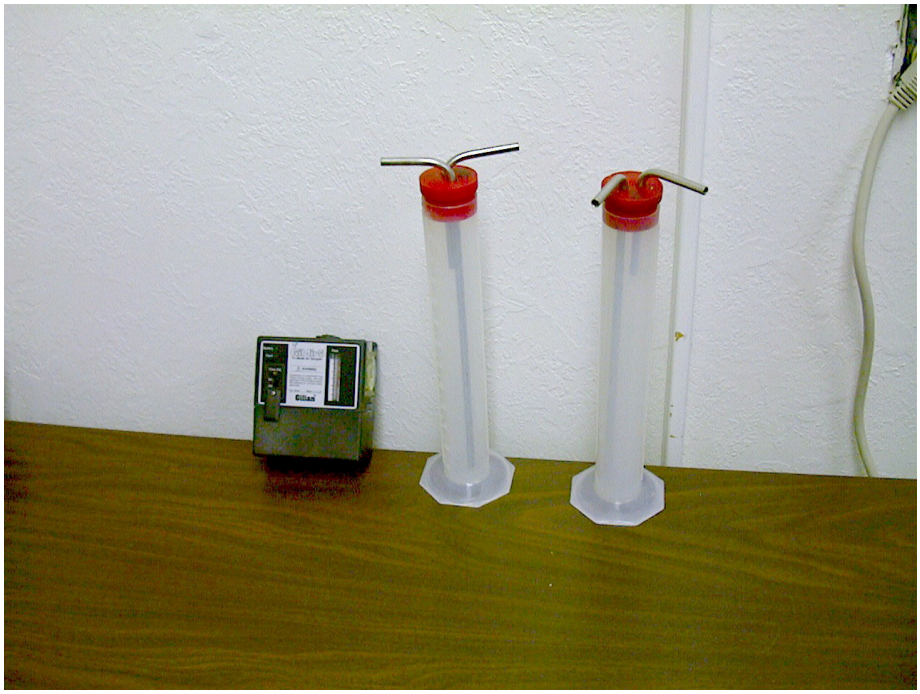

Figure 1. Tritium samplers and pump.

The sample input line was inserted through the sample port into the vault headspace. The pump was turned on, drawing air from the vault headspace through the deionized water. The removal efficiency of tritium in the water vapor phase into the deionized water was

estimated to be better than 99%. Twenty (20) ml of water from the sampler was poured into a 20 ml vial and labeled. Prior to sampling the next vault, the samplers were washed with fresh deionized water. This reduces the probability of any leftover water that may contaminate the next sample.

A sample of the deionized water used in the bubblers was used as a control sample for background correction. The control sample along with the 20 ml vial samples from the vault(s) was sent to the counting laboratory. The lab was provided the following information for each sample:

- total volume of air pulled through the bubbler
- total volume of water used in the sampler
- water lost through evaporation (if any)
- whether ethylene glycol was mixed with the water. (Ethylene glycol is used as an antifreeze to prevent the water in the bubbler from freezing in cold weather.)

The lab results contained three sets of information, the activity concentration, the 1-sigma uncertainty, and the minimum detection limit (MDL). To be considered "real," the result had to be a positive number (negative numbers indicate that the background count exceeded the actual count), at least two times the 1-sigma uncertainty and greater than the MDL; otherwise, the measurement was label BDL (below detection limit).

Errors in tritium concentration determination include errors due to the sampling method and radionuclide counting statistics error. Statistical errors are straightforward to determine and were generally small for detections a few times above the MDL. Sample collection errors have to do with the setup and performance of the sampling. Care was taken to ensure the pumps were calibrated to a 1 lpm flow rate, the samplers were cleaned with deionized water after each use, the vials were properly labeled and the correct information provided to the lab. An oversight in the setup and performance of the sampling process could result in considerable error. The first series of vaults were sampled in mid February, 2004. Weather conditions at the vaults were very cold with winds exceeding 20 mph on several days with wind chill factors well below zero. It became unbearable to handle the samplers much longer than 5 minutes. Individuals performing tritium sampling wore two pairs of rubber gloves. The outer pair of gloves was changed out after the sampler was cleaned (with deionized water) in preparation for sampling the next vault. 150 ml of deionized water was poured into each sampler as a standard baseline set up. The cold weather made it difficult to handle the samplers so there could be some errors associated with the sample set-up during those cold days.

Another type of error is associated with representativeness of the sample. It was assumed that the tritium concentration throughout the vault was evenly distributed, but such an assumption may not have been entirely realized during the sample collection process. For example, when some of the vaults were opened, a stream of air was heard entering the vault. This influx of air would have reduced the tritium concentration in the vault

headspace to a certain degree. In other cases, air was expelled from the vault when the cap was removed. Air egress would not have altered the H-3 concentration in the vault if the H-3 concentration inside the vault was uniform. However, concentration uniformity inside the vaults was not confirmed, so both air ingress and air egress could have had an effect on the representativeness of the samples.

The vault atmospheres were sampled in two time periods, in February, 2004 and also in May and June, 2004. The measured H-3 concentrations are shown in Table II.

Table II. Measured tritium concentrations in vault atmosphere.

Vault ID	H-3 DAC		Vault ID	H-3 DAC		Vault ID	H-3 DAC
E-6	0.12		F-26	0.013		C-54	0.0018
E-7	1.2		C-51	1.6		A-55	0.15
E-8	0.56		A-52	0.49		B-55	0.048
C-9	BDL		B-52	1.4		C-55	0.0022
C-11	BDL		C-52	1.5		A-56	0.99
C-15	BDL		A-53	0.36		B-56	0.78
C-16	BDL		B-53	0.73		C-56	0.13
B-17	BDL		C-53	2.5		A-57	0.59
C-17	BDL		A-54	0.25		C-57	0.72
C-18	BDL		B-54	1.3		C-58	1.2
C-21	BDL						

H-3 RELEASE FRACTION FROM FUEL

The ANL-E waste was generated from the destructive examination of fuel elements irradiated in the EBR-II reactor. A typical such fresh fuel element contained 80% uranium and 20% plutonium. The uranium was enriched to 60% U-235 and the plutonium contained 10% Pu-240. The burnup of the fuel elements ranges from a few percent of heavy metal (uranium and plutonium) to approximately 15% of heavy metal. ORIGEN2 [3] calculations were performed for a typical fuel element having the fresh fuel composition of

U-235 = 36 g U-238 = 24 g Pu-239 = 13.5 g Pu-240 = 1.5 g.

The fuel was irradiated to approximately 12% burnup with the FFTFC.LIB (Fast Flux Test Facility) cross-sections in the ORIGEN2 libraries, and decayed for two years that correspond to approximately the time when the RH TRU waste from the fuel element was packaged. At that time, the H-3 to Cs-137 activity ratio in the fuel, assuming no radionuclides were released from the fuel, was 7.1×10^{-3} (0.155 Ci of H-3 and 21.8 Ci of Cs-137).

Table I lists the estimated Cs-137 contents in each vault based on dose rate measurements on the stored drums at the time of their packaging. If all the H-3 co-produced with the Cs-137 during irradiation was retained by the fuel particles that adhered to the waste, the H-3 activity contents in the vaults would have been 7.1×10^{-3} times the Cs-137 activity

content. From these estimates of the theoretical total H-3 contents in the waste drums, theoretical total H-3 concentrations in the vault atmospheres were calculated, assuming that all the H-3 was released and retained inside the vaults. The free volume of a vault was calculated as the geometrical volume of the vault, based on dimensions shown in table I, less half of the volume of the drums. The 30-gal drums were assumed to be 20 in. in diameter and 30 in. high. The H-3 contents were decayed to April 1, 2004 from the package dates to compare with the measured results. The ratio of measured concentration to calculated theoretical total concentration is defined as the release fraction, as shown in Table III.

Table III. Comparison between calculated theoretical total and measured H-3 concentrations and H-3 release fraction to the vault atmosphere.

Vault ID	Theoretical total H-3 concentration (DAC)	Measured H-3 concentration (DAC)	Release fraction
E-6	1834	0.12	6.6E-05
E-7	3822	1.2	3.2E-04
E-8	1701	0.56	3.3E-04
C-9	2176	BDL	<1.0E-06
C-11	912	BDL	<1.0E-06
C-15	4328	BDL	<1.0E-06
C-16	2490	BDL	<1.0E-06
B-17	1749	BDL	<1.0E-06
C-17	2174	BDL	<1.0E-06
C-18	4018	BDL	<1.0E-06
C-21	2928	BDL	<1.0E-06
F-26	1296	0.013	1.0E-05
C-51	5870	1.6	2.7E-04
A-52	2247	0.49	2.2E-04
B-52	6365	1.4	2.2E-04
C-52	914	1.5	1.6E-03
A-53	2221	0.36	1.6E-04
B-53	1577	0.73	4.7E-04
C-53	4278	2.5	5.9E-04
A-54	3992	0.25	6.3E-05
B-54	911	1.3	1.4E-03
C-54	1367	0.0018	1.3E-06
A-55	2524	0.15	6.0E-05
B-55	3959	0.048	1.2E-05
C-55	255	0.0022	8.7E-06
A-56	2660	0.99	3.7E-04
B-56	4697	0.78	1.7E-04
C-56	2701	0.13	4.8E-05
A-57	4597	0.59	1.3E-04
C-57	2383	0.72	3.0E-04
C-58	2713	1.2	4.4E-04

The distribution of release fractions for the measured vaults is shown in Figure 2.

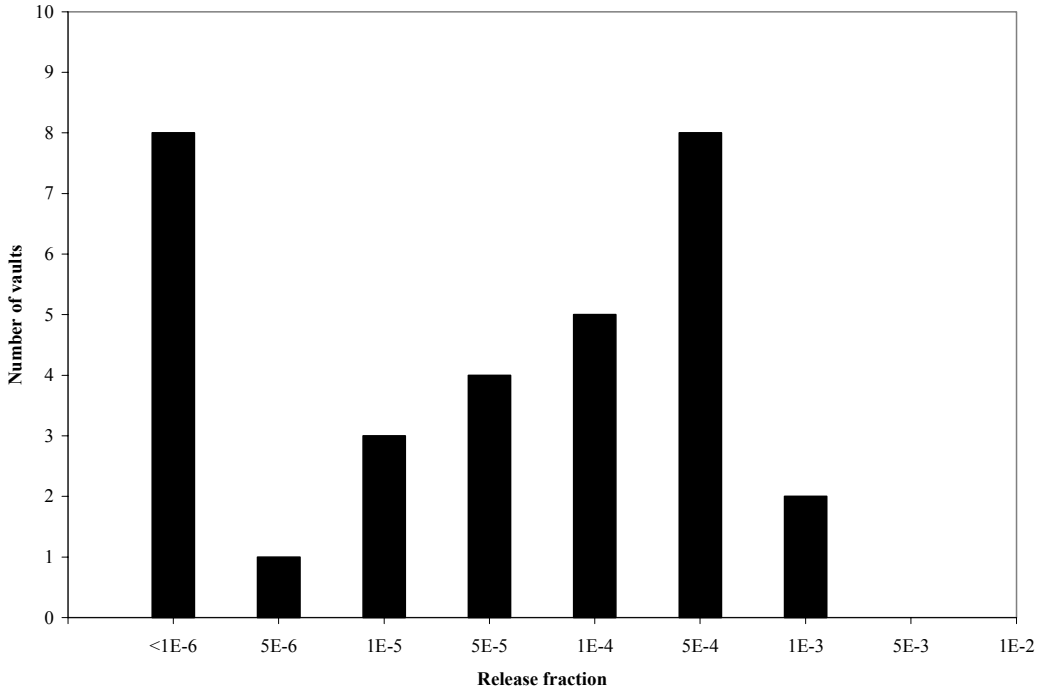

Figure 2. Distribution of H-3 release fraction to storage vaults.

DISCUSSION

The presence of tritium in sealed vaults that store RH TRU waste depends on many factors. First, the vaults have to be air-tight for many years. It may appear that this may be difficult to achieve. However, some recent measurements of air samples from the vaults also show the presence of radiolytic hydrogen, indicating that most of the vaults are indeed air-tight. Second, the fuel particles that adhere to the waste must have retained some of the tritium produced from fission at the time of waste packaging. This is somewhat surprising, given that the fuel particles were in the form of fine dust created during cutting, grinding, and polishing the fuel samples for examination. Third, tritium has to be able to diffuse out of the fuel grain slowly and then combine with oxygen to form tritiated water to be detected by the method discussed in this paper. The oxidation of tritium to tritiated water may be explained by the radiation environment in which the tritium may be ionized for combination with oxygen. The tritium diffusion rate out of the fuel grains has to low enough that some tritium remains in the fuel particles during waste production and high enough that over the 10 to 20 years in a sealed environment it becomes measurable in a sealed environment.

Both errors in estimating the tritium production from fission and measurements of its concentrations in air may have large errors. These errors are probably limited to a factor of 2 to 3. The deduced "release fraction," however, spans a range of more than three orders of magnitude. Therefore, it appears that the waste generation process and tritium

diffusion rates may be the dominant factors in determining how much tritium is released from the waste.

CONCLUSION

The detection of tritium in sealed storage vaults is somewhat surprising, given that the waste contained only minute particles of irradiated fuel that contained only small quantities of tritium from fission. The deduced release fraction of the total estimated tritium in the waste to vault atmosphere in the form of tritiated water vapor ranges from below the detection limit (1×10^{-6}) to as high as a few times 10^{-3}, but generally clusters around a few times 10^{-4}. At such release fractions, when the waste is stored in sealed vaults, the tritium levels in the vault atmosphere may reach radiologically significant levels, which have to be evaluated for tritium exposures when the vaults are opened.

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